

FORM PTO-1390 (REV 10-2000)		U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		GJE-230A U.S. APPLICATION NO. (If known, 37 CFR 1.5)	
INTERNATIONAL APPLICATION NO. PCT/GB00/03851		INTERNATIONAL FILING DATE October 6, 2000	PRIORITY DATE CLAIMED October 8, 1999
TITLE OF INVENTION Supported Homogeneous Catalysts For Selective Hydrogenation			
APPLICANT(S) FOR DO/EO/US Mark Joseph Burk, Arne Gerlach			
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ul style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)). 4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ul style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
<p>Items 11 to 16 below concern document(s) or information included:</p> <ul style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <ul style="list-style-type: none"> <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: Copy of Form PCT/RO/101 Copy of Form PCT/RO/144 Copy of Form PCT/RO139 			

C O P Y

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER	
09/700821	PCT/GB00/03851	GJE-230A	
<p>17. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</p> <p>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00</p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00</p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00</p> <p>International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00</p> <p>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00</p>		CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$ 860.00	
<p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).</p>		\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	14 - 20 =	0	X \$18.00
Independent claims	1 - 3 =	0	X \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		+ \$270.00	
TOTAL OF ABOVE CALCULATIONS =		\$ 860.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.		\$	
SUBTOTAL =		\$	
<p>Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).</p>		\$	
TOTAL NATIONAL FEE =		\$ 860.00	
<p>Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property</p>		+	
TOTAL FEES ENCLOSED =		\$ 860.00	
		Amount to be refunded:	
		\$	
		charged:	
		\$	
<p>a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>19-0065</u> in the amount of \$ <u>860.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>19-0065</u>. A duplicate copy of this sheet is enclosed.</p>			
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p>			
<p>SEND ALL CORRESPONDENCE TO:</p> <p>Mr. David R. Saliwanchik Saliwanchik, Lloyd & Saliwanchik A Professional Association 2421 N.W. 41st Street, Suite A-1 Gainesville, FL 32606-6669</p>			
<p><i>COPY</i></p> <p><i>David Saliwanchik</i></p> <p>SIGNATURE</p> <p>David R. Saliwanchik</p> <p>NAME</p> <p>31,794</p> <p>REGISTRATION NUMBER</p>			

09/700821
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November 20, 2000

Patent Application
Docket No. GJE-230A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : Mark Joseph Burk and Arne Gerlach
Docket No. : GJE-230A
For : Supported Homogeneous Catalysts For Selective Hydrogenation

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Please amend the above-identified application as follows:

In the Claims

Please amend the following claims:

Claim 2, line 1: Please delete "A" and insert --The--

Claim 3, line 1: Please delete "A" and insert --The--

Claim 4, line 1: Please delete "A" and insert --The--

Claim 5, line 1: Please delete "A" and insert --The--

Claim 6, line 1: Please delete "A" and insert --The--

Claim 6, line 1: Please delete "any preceding claim" and insert --claim 1--

Claim 7, line 1: Please delete “A” and insert --The--

Claim 8, line 1: Please delete “A” and insert --The--

Claim 8, line 1: Please delete “any preceding claim” and insert --claim 1--

Claim 9, line 1: Please delete “A” and insert --The--

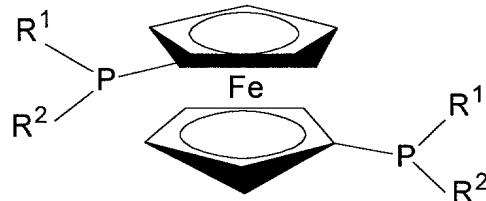
Claim 10, line 1: Please delete “A” and insert --The--.

Claim 10, line 1: Please delete “any preceding claim” and insert --claim 1--

Claim 11, line 1: Please delete “A” and insert --The--

Claim 12 (amended):

[Use of a catalyst according to any preceding claim, in a] A process of hydrogenating an aldehyde to produce the corresponding primary alcohol wherein said process utilizes a supported catalyst comprising a cationic rhodium (I) complex of the formula



wherein R¹ and R² are the same or different hydrocarbon groups of up to 30 C atoms, or R¹ and R² are linked to form a ring, and a heterogenous support medium that provides anionic binding sites.

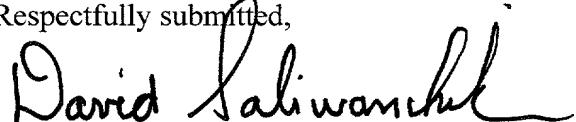
Claim 13, line 1: Please delete "Use" and insert --The process--

Claim 14, line 1: Please delete "Use" and insert --The process--

Claim 14, line 1: Please delete "or claim 13"

The Commissioner is hereby authorized to charge any fees under 37 CFR 1.16 or 1.17 as required by this paper to Deposit Account 19-0065.

Respectfully submitted,



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DRS/la

SUPPORTED HOMOGENEOUS CATALYSTS FOR
SELECTIVE HYDROGENATION

Field of the Invention

5 This invention relates to a supported catalyst and to its use, e.g. in the efficient and selective hydrogenation of aldehydes to alcohols.

Background of the Invention

Both homogeneous and heterogeneous catalysts are known, as are their respective advantages and disadvantages. One way of combining the features of both is to immobilise 10 or tether a homogeneous catalyst to a polymeric or inorganic solid support. An undesirable aspect of this strategy is that the heterogenised ligand systems often are very tedious and/or expensive to prepare. Another problem is that polymer-supported homogeneous catalysts frequently have reduced catalytic activities and selectivities relative to the unsupported homogeneous analogues. Upon attempted reuse, the activities and 15 selectivities of these catalysts are often reduced further. Finally, many immobilised homogeneous catalysts suffer from a high degree of metal loss from the support (leaching) during use; see, for example, Lindner, *et al, Angew. Chemie Int. Ed.* 1999, 38, 2155.

Aldehyde reduction often is a desirable step in obtaining valuable alcohol products from inexpensive starting materials (e.g., alkenes, hydrogen and carbon monoxide in the 20 case of hydroformylation). Despite the importance of aldehyde reduction in organic chemistry, surprisingly few generally applicable manufacturing methods are available for this transformation. Hydride reducing agents (e.g. LiAlH_4 or NaBH_4) are widely used, but are moisture-sensitive reagents that are not economically attractive for commercial 25 procedures since they are employed in stoichiometric quantities. Moreover, their use requires tedious work-up procedures and generates substantial quantities of waste (boron or aluminium salts).

Numerous heterogeneous catalysts, such as PtO_2 , Raney Ni, and Pd/C, can catalyse the reduction of specific aldehydes. However, heterogeneous catalysts are often intolerant of various organic groups such as divalent sulfides. Moreover, other sensitive groups such 30 as nitro, oxime, ketone, aryl halide or benzyloxy, also are reduced. Another problem encountered when reducing aromatic aldehydes using heterogeneous catalysts is that the

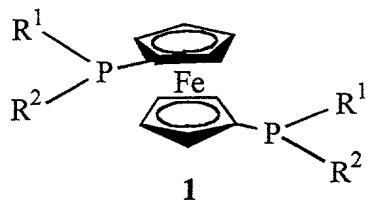
product may be further reduced to a methyl substituent. For example, heterogeneous hydrogenation of benzaldehyde often affords toluene.

Very few practical homogeneous systems efficiently catalyse aldehyde hydrogenation. Problems often encountered include low reaction rates and/or catalyst 5 deactivation due to aldehyde decarbonylation processes.

The use of cationic rhodium catalysts for aldehyde hydrogenation has been reported by Tani *et al*, *Chem. Lett.* 1982, 261, and by Burk *et al*, *Tetrahedron Lett.* 1994, 35, 4963. Results suggest that the achievement of high efficiency in rhodium-catalysed aldehyde hydrogenation requires the use of electron-rich (dialkyl- or trialkyl-substituted) 10 chelating phosphine ligands, but these tend to be very air-sensitive and are not suitable for industrial manufacture. Burk *et al*. describes an electron-rich, yet air-stable crystalline ligand, 1,1'-bis(diisopropylphosphino)ferrocene (DiPFc) 1 ($R^1 = R^2 = i\text{-Pr}$). The homogeneous rhodium catalyst (DiPFc-Rh) also is stable to oxygen and has been shown to hydrogenate a limited set of aldehydes with high reaction rates.

15

20



A new method of anchoring certain rhodium catalysts to solid supports has recently been described by Augustine *et al*, *Chem. Comm.* 1999, 1257. This simple procedure involves treating a readily available solid material (silica, alumina, carbon, etc.) with a 25 heteropolyacid such a phosphotungstic acid, followed by addition of an appropriate catalyst precursor complex. Immobilised catalysts formed in this fashion were reported to serve as active and reusable catalysts for alkene hydrogenation.

Summary of the Invention

According to the present invention, an immobilised homogeneous catalyst is useful, 30 *inter alia*, for the efficient and chemoselective hydrogenation of aldehydes. The catalyst system is based upon homogeneous rhodium complexes bearing phosphines of formula 1, wherein R^1 and R^2 are independently the same or different hydrocarbon substituents, e.g.

alkyl, substituted alkyl, arylalkyl or aryl, of up to 30 C atoms, or R¹ and R² are linked to form a ring. Preferably, R¹ and R² are alkyl groups and more preferably identical alkyl groups. The solid support provides anionic binding sites.

5 The utility of the novel catalyst is surprising, for various reasons. Firstly, it was not evident that the complex could be supported. Secondly, its activity for aldehyde hydrogenation is good especially given the acidic nature of the support. Further, the immobilised hydrogenation catalyst can be effectively recovered and re-used.

Description of the Invention

10 Solid supports that are effective for use in the invention are those providing anionic binding sites. The support may or may not be modified with a heteropolyacid anchoring agent. The support medium is preferably an oxide such as alumina, silica, carbon, montmorillonite, etc., and is preferably modified with a heteropolyacid. The heteropolyacid is preferably of the Keggin type, e.g. phosphotungstic acid, phosphomolybdic acid or silicotungstic acid. Alternatively, an anionic exchange resin such 15 as poly *para*-toluenesulfonic acid or Nafion in its acidic or anionic form may be used. For example, the support medium is a cation exchange resin containing sulphonic acid groups $-\text{SO}_3^- \text{X}^+$, wherein X⁺ is a proton or any other exchangeable cation. A preferred cation exchange resin is a tetrafluoroethylene-perfluoro(vinyl ether sulfonate) copolymer.

20 Many different types of aldehydes, e.g. of formula RCHO, wherein R is an organic group up to 30 C atoms, may be hydrogenated to give RCH₂OH, using the novel catalyst. The aldehyde substrate may possess a range of different functional groups that either inhibit or react with commonly employed heterogeneous catalysts. Due to the acidic nature of the supports used in the immobilisation of the homogeneous catalyst, a non-standard solvent mixture may be required. The use of an alcohol/water mixture, and 25 particularly an isopropanol/water mixture, is preferred, so that the hydrogenation reaction proceeds to completion. In particular, acetal formation can be minimised or avoided. The immobilised catalyst system may be recovered by simple filtration and re-used in subsequent reactions.

30 In addition to the hydrogenation of aldehydes, a catalyst of the invention may also be used for hydrogenation of other unsaturated groups. For example, unsaturated functionality such as the carbon-carbon double bond of alkenes, the carbon-carbon triple bond of alkynes, the carbon-oxygen double bond of ketones and the carbon-nitrogen

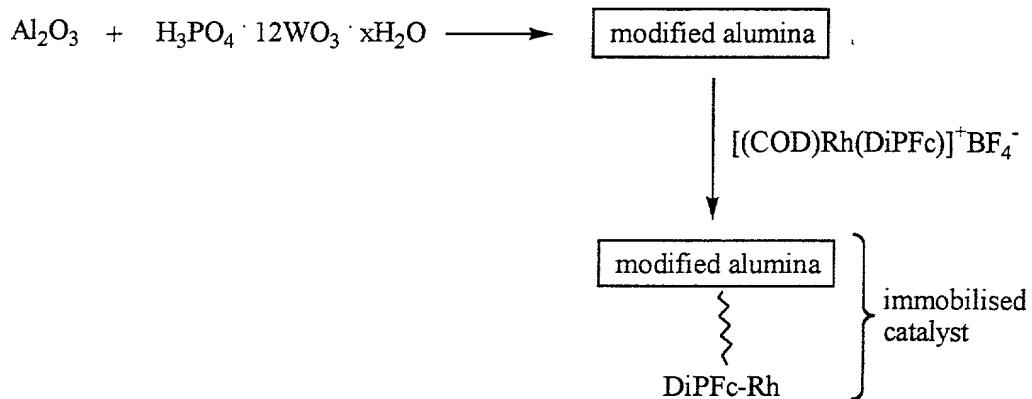
double bond of substrates such as N-acylhydrazones may be hydrogenated using these catalyst systems.

Some aldehydes are quite temperature-sensitive and decompose as the temperature is increased much above room temperature. In such cases, the ability to perform the 5 hydrogenation at mild temperatures is vital. Increasing the temperature may increase the reaction rate, but the novel catalyst may be performed over a broad temperature range of -30°C to +150°C. The preferred temperature is in the range 0°C to 60°C.

Performing reactions under low pressure is often preferred for manufacturing due to the fact that high-pressure equipment is more costly to purchase and operate. An 10 important advantage of this invention is that the catalyst can perform effectively under both high and low hydrogen pressures, e.g. over the range of 1 to 100 atmospheres (100 - 10000 kPa). Increasing the pressure may increase the reaction rates. The preferred pressure range will depend on the process being operated and the desired reaction rates.

Heterogenised rhodium catalyst systems bearing 1,1'-bis(dialkylphosphino)ferrocene ligands **1** may be prepared via various procedures. By way of representative example, an immobilised catalyst may be formed by mixing neutral alumina with phosphotungstic acid in methanol, followed by the addition of the catalyst precursor $[(\text{COD})\text{Rh}(\text{DiPFc})]^+\text{BF}_4^-$ (see Scheme 1). After allowing the mixture to stir for a specified period, the rhodium complex is completely absorbed onto the solid support. 20 The tethered catalyst is then filtered, washed with methanol, and employed directly in catalysis. The mechanism of absorption and the exact nature of the tethered complex are unclear.

Scheme 1.



The DiPFc-Rh catalyst prepared as in Scheme 1 has been tested for effectiveness in the hydrogenation of a range of different multifunctional aldehydes. These studies were aimed at demonstrating the combined properties of high catalytic efficiency under mild 5 conditions, selectivity in the reduction process, and tolerance of the catalyst to certain functionality. The robust nature of the catalyst system also was important. Moreover, comparisons have been made with commonly employed heterogeneous catalysts such as palladium on carbon, platinum oxide, and palladium on barium sulfate.

The following Examples illustrate the invention.

10 Example 1

Preparation of [(DiPFc)Rh(COD)]X on modified silica

A solution of phosphotungstic acid (PTA, 288 mg, 0.1 mmol, 1.0 eq.) in 25 ml degassed methanol was added dropwise to a vigorously stirred (overhead stirrer was used to minimise grinding) suspension of 4.00 g silica (Silica gel 60 for flash chromatography 15 (Fluka), particle size 0.035-0.070 mm (220-440 mesh ASTM, activity according to Brockmann and Schroder: 2-3) in 30 ml of degassed methanol under nitrogen. The resulting mixture was stirred for 1 hour at room temperature. Subsequently, a solution of [(DiPFc)Rh(COD)]BF₄ (64 mg, 0.09 mmol, 0.9 eq.) in 10 ml degassed methanol was dripped to the vigorously stirred slurry of the activated silica. Stirring was continued for 20 4.5 hours at room temperature. After solvent evaporation the remaining solid was placed in a Soxhlet apparatus and continuously extracted with degassed methanol under nitrogen for 16 hours. The orange silica powder was isolated, dried and stored under nitrogen as a precaution. Yield: 3.64 g (86%).

The alumina supported DiPFc-Rh catalyst was prepared by an analogous protocol 25 to that outlined above.

Example 2

General Hydrogenation Procedure

All reactions were carried out in a 50 ml Parr micro-reactor modified with an injection septum and valve. The micro reactor was used in connection with a suitable glass 30 liner. The solvent (2-propanol/water mixture; 1:1 v/v) was deoxygenated by bubbling nitrogen through it for 3 hours while stirring. The hydrogenation substrate and the immobilised catalyst were added to a 50 ml glass liner, which was then immediately placed

in a 50 ml Parr pressure vessel. This was then sealed and purged with hydrogen (5 pressurisation (690 kPa)/release cycles). Degassed solvent (2-propanol/water; 1:1 v/v) was then added *via* cannula, the reactor purged again with hydrogen (5 pressurisation (690 kPa)/release cycles), charged to the initial hydrogen pressure (690 kPa) and vigorously 5 stirred at a constant temperature (ambient temperature or heating bath). After an allocated period of time (hydrogen uptake was monitored) hydrogen pressure was released, and the reaction mixture was filtered (separation from the supported catalyst). The filtrate was then extracted several times with dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered and evaporated. The product distribution of the crude 10 product mixture was determined by $^1\text{H-NMR}$ spectroscopy and was compared with authentic samples of all products. In cases where the formation of water-soluble or volatile products was likely, the hydrogenation mixture also was analysed *via* HPLC prior to extractive work-up.

Thus, experiments were performed under a standard set of mild reaction 15 conditions: conversion to product = 100%, hydrogen pressure = 690 kPa, temperature = 20°C, reaction time = 16 h, mol aldehyde/mol Rh = 300-500 (based upon analysis of Rh content), concentration = 0.1 M, solvent: 2-propanol/water (1:1 v/v). Analytical procedures and results are given in Table 1.

The results show that the catalyst was robust and would operate effectively under 20 very mild reaction conditions. This is demonstrated by the fact that all experiments listed in Table 1 were conducted using catalyst that was stored under an atmosphere of air for a period of ten months. This immobilised homogeneous catalyst allowed complete hydrogenation of each aldehyde listed to afford exclusively the desired alcohol product in high yield. The results further reveal that aldehydes bearing either alkyl substituents (R = alkyl) or aromatic substituents (R = aryl) may be reduced with equal facility. Functional 25 groups that are reduced by most common heterogeneous catalysts, including aryl halide, nitro, and benzyloxy, were not reduced.

In contrast, common heterogeneous catalysts invariably yielded mixtures of products due to low chemoselectivity in reduction of the aldehyde carbonyl group 30 (substrates 7-9, 13). In all cases using the heterogeneous catalysts, milder than normal reaction conditions were employed in an effort to achieve some level of selectivity in the reduction process. This strategy provided the best advantage to the heterogeneous

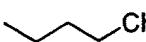
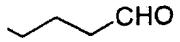
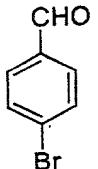
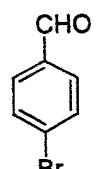
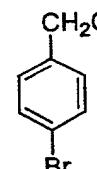
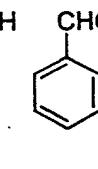
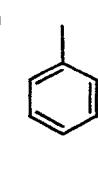
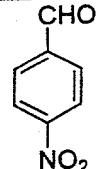
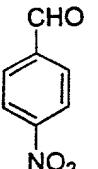
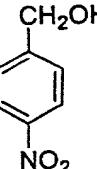
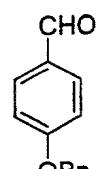
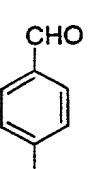
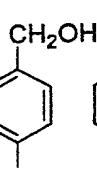
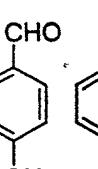
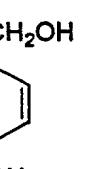
catalyst, but resulted in incomplete conversion of starting aldehyde in some cases. In all such cases, driving the reactions further to allow complete conversion of substrate led to lower selectivities.

Importantly, the novel catalyst displayed broad tolerance to various organic 5 functionalities, including sulphur-containing groups, with no apparent diminution of catalytic rates. Sulphur functionality is notoriously detrimental to most heterogeneous catalysts, leading to serious levels of catalyst inhibition. This point was amply demonstrated in experiments **10-13**. Of particular note is the successful hydrogenation of substrates **10** and **12**, which contain non-aromatic sulfide groups.

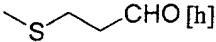
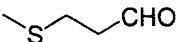
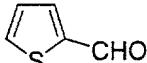
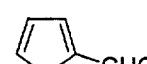
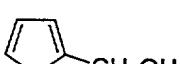
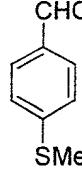
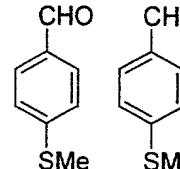
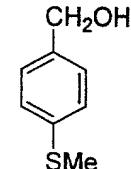
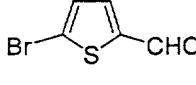
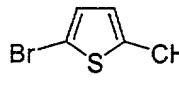
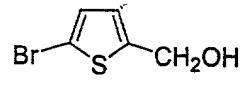
10 In addition to a catalyst with an alumina solid support, identical results were achieved using a DiPFc-Rh catalyst anchored to silica in the fashion described above in Scheme 1 (see hydrogenation results involving substrate **12**). The use of a silica support offers significant practical advantages since this immobilised catalyst system is more readily handled and removed from the reaction mixtures.

15 One advantage of an immobilised catalyst is the potential to remove it completely from the reaction mixture through filtration, and also to reuse the catalyst in subsequent processes. This is demonstrated by performing 4 successive hydrogenations involving 2-thiophene carboxaldehyde (substrate **11**). This particular aldehyde bears sulfur functionality, which should test the robustness of the immobilised catalyst in the presence 20 of potential coordinating groups. In each case the hydrogenation was performed under conditions described in Table 1. After allowing the reaction to stir for 6 h (hydrogen uptake was monitored), a small sample was removed, and complete conversion to alcohol product was confirmed by ¹H NMR spectroscopy. The entire solution phase containing the product then was removed by syringe, the catalyst was washed twice with fresh 25 solvent, and a subsequent aliquot of hydrogenation substrate in 2-propanol/water was added. The immobilised catalyst was used successfully for four catalytic cycles, and complete conversion to the corresponding alcohol product was observed after each run. No reduction of catalytic activity was noted over the four cycles.

Table 1. Selective Aldehyde Hydrogenations

	Catalyst ^[a]	Product Distribution ^[b]			
					
 6	DiPFc-Rh on alumina	n.d. ^[c]	100%		
 7	DiPFc-Rh on alumina				
	dppb-Rh on silica	93%	7%	n.d.	n.d.
	Platinum oxide	1%	90%	<1%	8%
	Pd on carbon	80%	n.d.	20%	n.d. ^[e]
	Pd on carbon ^[d]	n.d.	n.d.	n.d.	100% ^[e]
	Pd on barium sulfate ^[f]	85%	n.d.	15%	n.d. ^[e]
 8	DiPFc-Rh on alumina			nitro-reduced products	
	Pd on carbon	58%	0%	42%	
 9	DiPFc-Rh on alumina				
	Pd on carbon	n.d.	n.d.	40%	60%

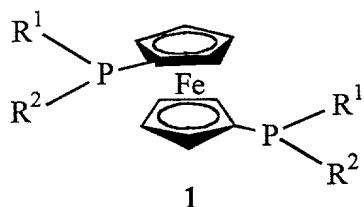
Catalyst^[a]Product Distribution^[b]

 10	Catalyst ^[a]	Product Distribution ^[b]	
			
	DiPFc-Rh on alumina	n.d.	100%
	Pd on carbon ^[i]	100%	n.d.
	Platinum oxide ^[i]	>98%	<2%
 11	Catalyst ^[a]	Product Distribution ^[b]	
			
	DiPFc-Rh on alumina	n.d.	100%
	Pd on carbon ^[i]	92%	8%
 12	Catalyst ^[a]	Product Distribution ^[b]	
			
	DiPFc-Rh on alumina	n.d.	100%
	DiPFc-Rh on silica	n.d.	100%
	DiPFc-Rh on silica ^[i]	n.d.	100%
	DiPFc-Rh on silica ^[k]	69%	31%
	dppb-Rh on silica	100%	0%
	Platinum oxide ^[i]	3%	97%
	Pd on carbon ^[i]	95%	5%
 13	Catalyst ^[a]	Product Distribution ^[b]	
			
	DiPFc-Rh on alumina	40%	60%
	Pd on carbon	17%	n.d.
			83%

[a] Hydrogenation conditions for DiPFc-Rh on alumina or silica: 100 psi hydrogen, S/C > 300, 0.1 molar in 2-propanol - water (1:1), room temperature, overnight; conditions for dppb-Rh on silica: 100 psi hydrogen, S/C > 200, 0.1 molar in 2-propanol - water (1:1), room temperature, overnight; conditions for platinum oxide: 1 bar hydrogen, 5 mg catalyst per mmol substrate, 0.1 molar 2-propanol - water (1:1), room temperature, 30 mins; conditions for palladium on carbon (10%): 1 bar hydrogen, 5 mg catalyst per mmol substrate, 0.1 molar in 2-propanol - water (1:1), room temperature, 30 mins. [b] Determined by $^1\text{H-NMR}$ analysis after extraction of the crude reaction mixture with dichloromethane, drying (sodium sulfate) and evaporation. [c] Not detected by $^1\text{H-NMR}$, GC or HPLC. [d] Reaction conditions: 100 psi hydrogen, 10 mg palladium on carbon (10%) per mmol substrate, room temperature, 1 hour. [e] Determined by HPLC analysis of the crude reaction mixture. [f] Reaction conditions: 1 bar hydrogen, 5 mg palladium on barium sulfate (5%) per mmol substrate, room temperature, 30 mins. [g] Detected by HPLC analysis of the crude reaction mixture. [h] Purchased from Fluka as a technical mixture of various amounts of monomers and oligomers. [i] Reaction conditions: 100 psi hydrogen, 10 mg palladium on carbon (10%) per mmol substrate, room temperature, 16 hours. [j] Reaction conditions: 100 psi hydrogen, S/C > 500, 60°C, 20 hours. [k] Reaction conditions: 100 psi hydrogen, S/C > 1000, 60°C, 24 hours. [l] Reaction conditions: 100 psi hydrogen, 10 mg platinum oxide per mmol substrate, room temperature, 16 hours.

CLAIMS

1. A supported catalyst comprising a cationic rhodium(I) complex of the formula



wherein R¹ and R² are the same or different hydrocarbon groups of up to 30 C atoms, or

10 R¹ and R² are linked to form a ring, and a heterogeneous support medium that provides anionic binding sites.

2. A catalyst according to claim 1, wherein the support medium comprises a heteropolyacid anchoring agent.

3. A catalyst according to 2, wherein the heteropolyacid is of the Keggin type.

15 4. A catalyst according to claim 3, wherein the heteropolyacid is phosphotungstic acid, phosphomolybdic acid or silicotungstic acid.

5. A catalyst according to claim 4, wherein the heteropolyacid is phosphotungstic acid.

20 6. A catalyst according to any preceding claim, wherein the support medium comprises an oxide selected from alumina, silica, titania, lanthana, zeolites and clays.

7. A catalyst according to claim 6, wherein the metal oxide is alumina.

8. A catalyst according to any preceding claim, wherein the support medium is a cation exchange resin containing sulphonic acid groups $-\text{SO}_3^-\text{X}^+$, wherein X⁺ is a proton or any other exchangeable cation.

25 9. A catalyst according to claim 8, wherein the cation exchange resin is a tetrafluoroethylene-perfluoro(vinyl ether sulfonate) copolymer.

10. A catalyst according to any preceding claim, wherein R¹ and R² are each an alkyl group.

11. A catalyst according to claim 10, wherein R¹ = R² = *i*-Pr.

30 12. Use of a catalyst according to any preceding claim, in a process of hydrogenating an aldehyde to produce the corresponding primary alcohol.

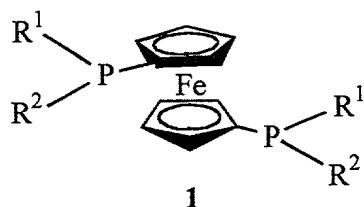
13. Use according to claim 12, wherein substrate conversion of at least 90% is effected, and wherein the aldehyde also contains at least one sulfide group that is retained in the product.
14. Use according to claim 12 or claim 13, wherein the process is carried out in a mixture of water and an alcohol.

ABSTRACT

SUPPORTED HOMOGENEOUS CATALYSTS FOR
SELECTIVE HYDROGENATION

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A supported catalyst comprises a cationic rhodium(I) complex of the formula



wherein R¹ and R² are the same or different hydrocarbon groups of up to 30 C atoms, or

15 R¹ and R² are linked to form a ring, and a heterogeneous support medium that provides anionic binding sites.

Such a complex is particularly useful as a catalyst in a process of hydrogenating an aldehyde to produce the corresponding primary alcohol.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C 1001 and that such willful false statements may jeopardise the validity of the application or any patent issued thereon.

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DECLARATION AND POWER OF ATTORNEY

As a below-named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of subject matter which is claimed and for which a patent is sought on an invention entitled
SUPPORTED HOMOGENEOUS CATALYSTS FOR SELECTIVE HYDROGENATION

the specification of which is attached hereto or

was filed on 06 OCT 2000 as United States Application Number or PCT International Application Number PCT/GB00/03851 and was amended on (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for a patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application Number(s)	Country	Foreign Filing Date	Priority Not Claimed	Certified Copy Attached?
			YES	NO
9923952.7	GB	08 OCT 1999	<input type="checkbox"/>	<input type="checkbox"/>
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			<input type="checkbox"/>	<input type="checkbox"/>

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:
91
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